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MINERALOGY.—*Tschermigite (Ammonium Alum) from Wyoming.*

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INTRODUCTION

A sample of mineral to be tested for potash was received from Mr. C. R. McGregor of the firm of McGregor Brothers Company, contractors and builders, Ogden, Utah. The mineral was identified as tschermigite, natural ammonium alum, and as far as known is the first reported occurrence of this mineral in America. Mr. McGregor has kindly furnished information regarding the deposit of the mineral; it is located about 5 kilometers (3 miles) south of Wamsutter, and 65 Km. (40 miles) west of Rawlins, Wyoming, both places being on the Union Pacific Railroad. The mineral occurs in a 2 meter ledge of black shale and is traceable along the brink of the hills for nearly 5 km. (3 miles).

The writer wishes to express his thanks to Dr. W. T. Schaller for his cooperative interest in the work and preparation of this paper.

ASSOCIATION AND PROPERTIES

In the specimens received by the Geological Survey, tschermigite forms the cementing material holding together seams of pure tschermigite, fragments of brown bituminous shale, nodules of yellow jarosite and a few scattered gypsum crystals. The cementing tschermigite is intimately mixed with the shale fragments and associated minerals. Many of the smaller pieces of shale are rudely rectangular in shape and where these have fallen away, cubic cavities remain in the compact tschermigite. An abundance of pure material suitable for analysis, could readily be obtained from the seams.

The jarosite coats, and in places is inclosed in, the alum, and also forms small pure nodular masses. It is pale yellow in color and very

[1] Published by permission of the Director, U. S. Geological Survey. Received November 3, 1921.

fine grained, the individual crystals and their rhombohedral character being recognized only under the highest magnifying power of the petrographic microscope. The probability of this jarosite containing ammonia was suggested. A carefully selected sample was obtained largely from the small nodular masses. Treatment with water at room temperature (near 25° C.) yielded 0.87 per cent soluble matter, consisting of some tschermigite, together with a small quantity of jarosite, and a trace of organic matter. If it be considered that the water-soluble content of the jarosite is practically all tschermigite the 0.87 per cent soluble matter would contain only 0.05 per cent ammonia as $(NH_4)_2O$. The jarosite sample was found to contain 1.30 per cent $(NH_4)_2O$, which when corrected for the ammonia in 0.87 per cent of admixed tschermigite, gave 1.25 per cent for the pure jarosite. A lack of suitable material prevented further work being done other than to establish quantitatively the presence of considerable potash and a slight amount of soda. As far as know this is the first recorded occurrence of an ammoniacal jarosite. The small amber colored gypsum crystals are not very abundant and do not present any evidence of unusual composition.

The tschermigite is colorless or white in thick masses and has a clear glassy appearance in small pieces. The mineral is isotropic and the broken pieces do not show any cleavage. The refractive index was found to be 1.457 and the density 1.645. Cornu[2] found the density of the Dux, Bohemia, tschermigite to be 1.636. The artificial ammonium alum has the density 1.626. The value 1.50 given for tschermigite in Dana's System of Mineralogy is obviously too low.

In some of the cavities are small incomplete crystals of tschermigite and some of the columnar masses have a large number of minute facets of the same crystal form along their side. Crystal faces are also present on top of parts of the seams, but nowhere were complete crystals evident. The incomplete crystals were seldom larger than one or two millimeters. The forms noted are $a(100)$, $o(111)$ and $d(110)$, all developed nearly equally, but with a very nonequal development of the different faces of a form on the same crystal.

CHEMICAL COMPOSITION

The mineral readily fuses in its own water of crystallization below the boiling point of toluene (105° C.). It is easily soluble in cold water and gives the usual reactions for ammonium alum. The

[2] Reference given under analysis III.

quantitative analyses were made on a uniform sample of carefully selected material which was practically free from associated mineral and gangue.

The average results obtained are tabulated below (I), together with the theoretical composition of ammonium alum [$Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$] (II), and analyses of the mineral from Bohemia (III, IV).

TABLE 1.—ANALYSES OF TSCHERMIGITE

	I	II	III	IV
	Average analysis of tschermigite from Wyoming	Composition of [$Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$]	Tschermigite from Dux, Bohemia	Tschermigite from Brüx Bohemia
Al_2O_3.....	11.57	11.28	11.40	11.39
$(NH_4)_2O$....	5.23	5.74	5.86[a]	5.62
Na_2O	0.21	.....	} 0.06	} 0.17
K_2O.....	Trace	.....		
MgO.....	0.13	.....	.....	.....
SO_3.....	35.11	35.33	34.99	35.14
H_2O.....	47.82	47.65	[47.69[a]]	[47.59[b]]
Insol.....	0.06	.....	.....	0.08
Fe_2O_3,CaO,Cl	Trace	.....	.....	0.01[c]
Total	100.13	100.00	100.00	100.00

[a] Given as 3.83 per cent $(NH_4)_2O$, but obviously an error, the 3.83 per cent representing NH_3. The value has been changed to its equivalent (5.86) for $(NH_4)_2O$. The water content given as 49.72 has been correspondingly corrected to 47.69.

[b] Given as 3.67 per cent NH_3 which has also been changed to its equivalent value of 5.62 per cent $(NH_4)_2O$. A correction has likewise been made of the reported water percentage, 49.54 obtained by difference, to 47.59 per cent.

[c] Fe_2O_3.

Analysis III; Deichmüller, J. V., *Neues Vorkommen von Ammonium-alaun.* Sitzb. d. n. Ges. Isis, Dresden, **1885,** 33. Analysis by Geissler. Locality, Vertrau auf Gott mine near Dux, Bohemia. This occurrence is also described by Cornu, F., *Tschermigite von Schellenken bei Dux in Böhmen.* Centr. Min. Geol. **1907,** 467–468.

Analysis IV; Sachs, A., *Über ein neues Tschermigitvorkommen von Brüx in Böhmen, etc.* Centr. Min. Geol. **1907:** 465–467. Locality, Guidoschacht in Nieder-Georgental near Brüx, Bohemia.

A set of four earlier analyses, by Gruner, Pfaff, Lampadius, and Stromeyer, showing similar results, are given by Rammelsberg, in his *Handbuch d. Mineralchemie,* p. 285 (1860). Natural ammonium alum also occurs at Tschermig, Bohemia (from which place the mineral is named); and has been reported from Tokod near Grau, Hungary; Saalfeld in Thuringia; in crater of Mt. Etna with other sulfates; and at Solfatara at Pozzuoli.

The ammonia was determined by the direct distillation of the sample in the customary Kjeldahl apparatus. A gram sample was dissolved in a 500 cc. Kjeldahl flask with 150 cc. of distilled water, an excess strong NaOH solution was then added with the usual precautions and 75 cc. of distillate were slowly received into 25 cc. N/10 H_2SO_4.

The excess of acid in the distillate was titrated with N/10 NaOH solution, using methyl orange indicator, the neutralization value of the distilled ammonia being obtained by difference and its percentage computed. Duplicate determinations agreed closely and were corrected for a blank test made on all reagents used.

The mineral was dried to constant weights at temperature intervals between 105° C. and 410° C. inclusive, with the following results. At 105° C. a loss of 36.48 per cent was obtained, which is slightly over three-fourths of the total percentage of water. At 200° C. the remaining water, excepting about one per cent of the total, was given off. At 350° C. a few tenths of one per cent of water are still retained in the residue. Losses in excess of the actual percentage of water commenced near 360° C. and became about three per cent at 410° C. Evidently ammonium sulfate in the double compound commences decomposition near 360° C. which is about 80° C. higher than the decomposition temperature of pure ammonium sulfate.

TABLE 2.—THE LOSS OBTAINED BY HEATING TSCHERMIGITE

Temperature		Percentage of loss	
Toluene bath	(105° C.)	36.48	
Air bath	125° C.	38.07	
	200° C.	47.10	
	215° C.	47.18	
	250° C.	47.26	
	310° C.	47.26	
	350° C.	47.58	Percentage of water in mineral 47.82
	360° C.	47.93	
	410° C.	50.62	

The strongly ignited residue gave a total loss of 88.06 per cent. This loss consisted of the water and ammonia [$(NH_4)_2O$] content together with nearly all of the sulfuric anhydride, a slight amount (0.10) being retained.

In order to interpret correctly the function of the small quantity of substances besides Al_2O_3, retained in the ignited residue, some comparative experiments with a prepared sodium alum were carried out. The percentage of strongly ignited residue from sodium alum was found to be nearly identical with the sum of the percentages of Na_2O

plus Al_2O_3. The average results on the prepared sodium alum are as follows:

TABLE 3

PARTIAL ANALYSIS, THEORETICAL COMPOSITION AND IGNITION RESULTS OF SODIUM ALUM.

Partial analysis of the prepared sodium alum		Theoretical percentage of Na_2O + Al_2O_3	Residue obtained by strong ignition	Theoretical percentage of Na_2SO_4 + Al_2O_3.
Na_2O.....	6.96			
Al_2O_3.....	11.07	17.91	17.78	26.64
Total.....	17.76			

Although the ignited residue from the sodium alum contained a small quantity of sulfate which compensates for the loss of a small quantity of volatilized alkali, the result seems to indicate the formation of a sodium aluminate, since in the ignited residue practically all of the sulfate radical is volatilized.

The partial elimination of SO_3 from Na_2O in the ignited residue of tschermigite is thus explained. It is possible that the small amount of $MgSO_4$ in the tschermigite residue reacts in a similar way with the Al_2O_3. However $MgSO_4$ alone in small quantities will dissociate considerably into MgO and SO_3 in the temperature of the ordinary strong blast.

The percentage of water was obtained by subtracting the sum of the $(NH_4)_2O$ and the volatilized SO_3 (the total percentage of SO_3 corrected for SO_3 retained in the ignited residue) from the total loss on ignition. The average results for tschermigite are tabulated below.

TABLE 4.—TOTAL WATER CONTENT OF TSCHERMIGITE

$(NH_4)_2O$.....		5.23
Total SO_3.....	35.11	
SO_3 retained in the ignited residue...	0.10	
Volatilized SO_3.....		35.01
		40.24
Total loss upon ignition.....		88.06
Subtracting the total of $(NH_4)_2O$ and volatilized SO_3.....		40.24
Water by difference.....		47.82
IGNITED RESIDUE OF TSCHERMIGITE		
Residue upon ignition.....		11.94 per cent
Sum of constituents other than Al_2O_3.....		0.50
Al_2O_3 by difference.....		11.44 per cent
Al_2O_3 by direct determination.....		11.57 per cent

The percentage of residue obtained was corrected for the minor nonvolatile constituents, as follows: Na_2O, 0.21 per cent; MgO, 0.13 per cent; nonvolatile insoluble matter, 0.06 per cent, and SO_3 retained in the residue, 0.10 per cent; the sum of which is 0.50 per cent.

BOTANY.—*On the species of* Dalbergia *of Mexico and Central America.* H. PITTIER.[1]

As considered in the light of modern taxonomy, the genus *Dalbergia* includes the former genera *Amerimnon* and *Ecastophyllum*. There is no generic difference between *Amerimnon*, established by Browne in 1756 to include Dalbergias with samaroid pods, and *Ecastophyllum* of the same author and date, containing the species with nummular pods. On the other hand, on the evidence of the generic definition, the species of *Amerimnon* do not fit into *Ecastophyllum*, and species of *Ecastophyllum* cannot come under *Amerimnon*.

In 1781, Linnaeus filius described his new genus *Dalbergia*, which under both the International and the American Rules would not be valid, but for the fact that neither of the two names having the priority really represents a generic entity, but only one part of a single genus, while the later name was intended to apply to both parts.

In this paper, therefore, in accordance with the well founded conclusions given by Prain[2] in his extensive monograph "*The Species of* Dalbergia *of South Eastern Asia*," the name *Dalbergia* is retained to designate the genus; *Amerimnon* becomes the name of a subgenus, while the species of *Ecastophyllum* are transferred to a single section of the same. This is the view accepted by all European botanists and, I believe, by the majority of those on this side of the Atlantic. In all the recent literature on the subject, including the description of a large number of species old and new, the same name is used, so that the resuscitation of *Amerimnon* as a substitute for *Dalbergia* would cause a great and useless confusion, even omitting the fact that it cannot be applied to the genus as understood today.

In its original form, the present paper included full descriptions of all Mexican and Central American species. Circumstances now have made it necessary to suppress the descriptions of old species and to reduce the paper to a simple enumeration of them, with their known distribution, and to descriptions of only the proposed new species. In addition, the following key has been prepared.

[1] Received December 15, 1921.

[2] Ann. Bot. Gard. Calc. **10**: 10–11. 1904.

KEY TO THE MIDDLE AMERICAN SPECIES OF DALBERGIA

Standard blade straight or hardly reflexed; style short and thick (*Sissoa*).

Leaflets ovate or oblong-lanceolate, rather large (3 to 11 cm. long); stamens 9.

Flowers about 5.5 mm. long, the standard obovate, subauriculate at the base; leaflets 3 to 8 cm. long, 1.5 to 2.5 cm. broad. 1. *D. cubilquitzensis.*

Flowers about 3.5 mm. long, the standard ovate or oblong, attenuate at the base; leaflets 4 to 11 cm. long, 2 to 5 cm. broad. 2. D. *tucurensis.*

Leaflets ovate or ovate-long, rather small (seldom over 4 cm. long); stamens 9 or 10.

Stamens 9.

Inflorescences loose, dichotomous-paniculate; flowers about 4 mm. long; leaflets ovate, obtuse or subacuminate. Ovary 1-ovulate; standard suborbiculate. 3. *D. melanocardium.*

Inflorescences congested, cymose-paniculate.

Flowers 3 to 3.5 mm. long; ovary glabrous, 2 or 3-ovulate; leaflets 3 to 5 cm. long. 4. *D. glomerata.*

Flowers about 5.5 mm. long; ovary hairy, 1 or 2-ovulate; leaflets 0.5 to 3 cm. long. 5. *D. congestiflora.*

Stamens 10.

Pistil glabrous.

Ovary 4 or 5-ovulate; wings narrow, elongate, the base of the blade truncate, 2-auriculate; leaflets oblong or obovate, whitish and rufo-reticulate beneath. 6. *D. tabascana.*

Ovary 1 or 2-ovulate; wings oblique, obovate, 1-auriculate; leaflets ovate, emarginate, ferruginous-pubescent beneath. 7. *D. cibix.*

Pistil more or less hairy. Ovary 2 or 3-ovulate.

Flowers 5 mm. long, the pedicels 1 mm. long or less; ovary minutely pubescent; standard subauriculate. 8. *D. mexicana.*

Flowers 10.5 mm. long, the pedicels 2.5 to 3.5 mm. long; ovary hairy on the margins; standard attenuate at the base. 9. *D. campecheana.*

Standard blade reflexed (with one exception, *D. brownei*, but then leaves 1-foliolate); style slender, often subulate (*Amerimnon*).

Flowers not over 12 mm. long; style geniculate, short and straight; legume orbicular and 1-seeded, or ovate-oblong and 1 to 3-seeded (*Ecastophyllum*).
Legume ovate-oblong, rounded at the apex, 1 to 3-seeded; flowers about 11 mm. long; standard obovate, straight; leaves 1-foliolate; stamens 10. 10. *D. brownei.*
Legume orbicular, 1 - seeded; standard orbiculate, reflexed.
Leaves 1-foliolate; flowers about 10 mm. long; stamens 10. 11. *D. ecastophyllum.*
Leaves 3 to 5-foliolate; flowers about 6 mm. long; stamens 9. 12. *D. monetaria.*
Flowers not less than 14 mm. long; style long and strongly arcuate; legume more or less lanceolate, 1 to 5-seeded. Stamens 10 (*Miscolobium*).
Leaves entirely glabrous, 5 to 7-foliolate, the leaflets 3 to 4 cm. long. 13. *D. calycina.*
Leaves more or less pubescent, 7 to 15-foliolate.
Leaves and pods hardly changing color in desiccation; leaflets 7 to 11, ovate, glaucous beneath; legume 1 to 5-seeded, rounded-obtuse at the apex. 14. *D. hypoleuca.*
Leaves and pods turning black in desiccation.
Leaflets suborbiculate or broadly ovate, not over 5 cm. long, the margin not revolute. 15. *D. granadillo.*
Leaflets ovate or oblong, up to 10.5 cm. long, the margins revolute.
Flowers about 15 mm. long, the pedicels 4 to 5 mm. long; standard suborbiculate, more or less emarginate at the base. 16. *D. retusa.*
Flowers about 16 mm. long, the pedicels about 5 mm. long; standard ovate or oblong, attenuate at the base. 17. *D. lineata.*

ENUMERATION OF SPECIES

1. Dalbergia cubilquitzensis (Donn. Smith) Pittier.

Dalbergia variabilis var. *cubilquitzensis* Donn. Smith, Bot. Gaz. **57:** 417. 1914.

TYPE LOCALITY: Cubilquitz, Alta Verapaz, Guatemala, altitude about 350 m.(*von Tuerckheim* 4091).

OTHER SPECIMENS EXAMINED:

GUATEMALA: Los Amates, Department Izabal, 1905, *Kellerman* 4789.

This species, considered by Mr. Donnell Smith as a mere variety of *D. variabilis* Vogel, differs from this in the pubescence, the shape and size of the

calyx lobes, the shape of the petals, the number of stamens, the shape and size of the leaves and leaflets, etc.

2. Dalbergia tucurensis Donn. Smith, Bot. Gaz. **46:** 111. 1908.
TYPE LOCALITY: Concepción near Tucuón, Alta Verapaz, Guatemala (*von Tuerckheim* II. 1712).

3. Dalbergia melanocardium Pittier, sp. nov.

Medium sized tree; branchlets terete, ferruginous pubescent, later glabrate and grayish.

Leaves 7 to 11-foliolate, the rachis terete, minutely pilosulous, 4 to 13 cm. long. Leaflets subcoriaceous, the petiolules sparsely ferruginous-pubescent, 3 to 4 mm. long, the blades ovate, rounded or subacute at the base, obtuse and subretuse at the apex, 1.5 to 4.5 cm. long, 1.3 to 2.5 cm. broad, dark green and pilosulous above, paler or rufescent, ferruginous-pubescent and reticulate beneath, the very slender veins prominent on both faces.

Inflorescences paniculate, axillary and terminal, congested, shorter than the leaves, the branched rachis ferruginous-pubescent. Bractlets small, ovate or orbiculate, ferruginous-pubescent. Flowers sessile or short pedicellate, about 4 mm. long. Calyx subbilabiate, broad, fulvous-hairy, about 2.5 mm. long, the two vexillar lobes broad and rounded, the 2 lateral ones equally long and obtuse, but narrower, the carinal one about twice longer, obtuse or bilobulate. Petals glabrous; standard suborbiculate, the claw oblique, 0.8 to 0.9 mm. long, the blade subbiauriculate at the base, emarginate at the apex, about 3 mm. long and broad; wings free from the keel, auriculate on both margins at the base, obtuse at the apex, about 4 mm. long (including the claw) and 1.4 mm. broad; carinal petals broader than the wings, ovate, auriculate on the vexillar side, obtuse, about 3.8 mm. long, 1.5 mm. broad. Stamens 9, monadelphous, the staminal tube glabrous, open above. Pistil 4.5 to 5 mm. long, the ovary stipitate, 1-ovulate, ferruginous-villous, the style thick, arcuate, glabrous, the stigma inconspicuous.

Type in the U. S. National Herbarium, no. 258410, collected at Ojo de Agua, Department of Santa Rosa, Guatemala, altitude about 900 meters, May, 1892, by Heyde and Lux (J. D. Smith 3295).

Known among the natives under the name of "Ebano," and distributed as *Dalbergia variabilis* Vogel. Like this species it has a calyx with two broad more or less connate upper lobes, and three narrower lower lobes, the middle (carinal) one about twice longer, but obtuse or retuse. But the flowers are sessile, shorter and broader, there are 9 stamens, the ovary is densely villous-hairy and the congested inflorescence is not cymose.

4. Dalbergia glomerata Hemsl. Diag. Pl. Nov. **1:** 8. 1878.
TYPE LOCALITY: Sangolica, Mexico (*Botteri* 1027).

5. Dalbergia congestiflora Pittier, sp. nov.

Small tree, 3 to 4 m. high; branchlets terete, striate, sparsely lenticellate, at first minutely grayish-pubescent.

Leaves 7 to 13-foliolate, the rachis slender, sparsely pubescent, 4 to 11 cm. long. Leaflets subcoriaceous, the petiolules pilosulous, 2 to 3 mm. long, the blades ovate-oblong, broadly cuneate at the base, rounded, slightly emarginate and sometimes mucronulate at the apex, 0.5 to 3 cm. long, 0.3 to 2.3 cm. broad, sparsely pilosulous on both faces, reticulate and with the venation prominulous above, beneath lineate-reticulate, the costa and veins prominent.

Inflorescences paniculate, cymose-branched, axillary or terminal on defoliate branchlets, congested, not over 3 cm. long, the rachis densely ferruginous-hairy. Bracts and bractlets oblong, ferruginous-hairy, very small, caducous. Flowers pedicellate, 5.5 mm. long, the pedicels 1 to 1.5 mm. long. Calyx subcampanulate, 2 to 2.5 mm. long, sparsely pubescent, the 2 vexillar lobes broad, rounded and adnate, the lateral lobes narrower and acute, the carinal lobe apiculate and longer. Petals glabrous; standard ovate or oblong, more or less attenuate at the base, emarginate at the apex, 3.6 mm. long, 1.4 to 1.6 mm. broad; wings elongate, oblique, more or less attenuate at the base, rounded at the apex, about 3 mm. long, 0.9 to 1.1 mm. broad; carinal petals ovate, auriculate on the vexillar side, obtuse at the apex, the claw about 0.8 mm. long, the blade about 2.5 mm. long, 1.5 to 1.8 mm. broad. Stamens 9, glabrous. Pistil 2.5 to 3 mm. long, hairy, ciliate on the margins, the ovary 1-ovulate (?), the style short and thick, the stigma inconspicuous.

Type in the U. S. National Hebarium, no. 381855, collected on lava fields near Cuernavaca, Morelos, Mexico, altitude about 1650 m., March 17, 1899, by C. G. Pringle (no. 6981).

Distributed as *Dalbergia glomerata* Hemsley, but the leaves are much smaller, the leaflets less numerous, more than half smaller, pilosulous on both faces, the flowers are larger, the standard is sensibly longer than the wings and keel and not suborbiculate but ovate or distinctly oblong, the ovary is apparently 1-ovulate, etc.

6. Dalbergia tabascana Pittier, sp.

Shrub (?); branchlets grayish, sparsely lenticellate, at first minutely grayish-pubescent.

Leaves 6 or 7-foliolate, the rachis slender, minutely pilosulous, 3 to 3.5 cm. long. Leaflets subcoriaceous, the petiolules minutely pubescent, 1 to 1.5 mm. long, the blades oblong or obovate, rounded at the base and apex, 1 to 2.5 cm. long, 0.5 to 1 cm. broad, dark green and glabrous above, whitish or rufescent, rufo-reticulate and minutely pilosulous beneath.

Inflorescences few-flowered, subcymose, axillary or paniculate at the end of the branchlets, the rachis branched, sparsely gray-pubescent. Bracts and bractlets ovate-oblong, pubescent, not over 1 mm. long, caducous. Flowers pedicellate, about 9 mm. long, the pedicels minutely gray-pubescent, 2 to 4 mm. long. Calyx tubular-campanulate, 3.5 to 4 mm. long, sparsely pubescent or glabrescent at the base, pubescent on the lobes, subbilabiate, the carinal lobe apiculate, not much longer than the vexillar ones, these obtuse, the lateral ones smaller and acute. Petals glabrous; standard obovate-oblong, straight, attenuate and subauriculate at base, rounded and slightly emarginate at apex, the claw about 2 mm. long, the blade 5.5 mm. long, 1.6 mm. broad; wings elongate-oblong, auriculate on the vexillar side, subauriculate on the carinal side, rounded at apex, the claw 2 mm. long, the blade about 5.5 mm. long, 1.6 mm. broad; carinal petals falcate, auriculate on the vexillar side, obtuse at the apex, the claw 2.2 mm. long, the blade about 4 mm. long and 1.8 mm. broad. Stamens 10, monadelphous, glabrous, alternately short and long. Pistil about 6 mm. long, glabrous, the ovary long-stipitate, 4 or 5-ovulate, the style oblique, straight, the stigma subcapitellate.

Type in the John Donnell Smith Herbarium, collected in inundated places near Mayito, Tabasco, Mexico, August 17, 1889, by J. N. Rovirosa (no. 583).

The type specimen is labelled *Dalbergia campecheana* Benth., but the leaves are small, with few, distinctly petiolulate leaflets, the inflorescences are few-flowered, the ovary is 4 or 5-ovulate, etc.

7. Dalbergia cibix Pittier, sp. nov.

Scandent shrub or vine, ascending to 20 m. above the ground; branchlets terete, grayish, more or less lenticellate, at first densely ferruginous-pubescent.

Leaves 7 to 9-foliolate, the rachis terete, slender, ferruginous-hirtous, 4 to 5 cm. long. Leaflets submembranous, the petiolules ferruginous-pubescent, about 1.5 mm. long, the blades ovate, rounded at the base, rounded and slightly emarginate at the apex, 1 to 2 cm. long, 0.6 to 1.3 cm. broad, sparsely pilosulous and minutely reticulate above, beneath densely ferruginous-pubescent, the costa prominent and the veins impressed; margins revolute.

Inflorescences paniculate, many-flowered, axillary, terminal or more or less fasciculate on defoliated nodes, the rachis branched, ferruginous-hairy. Bracts and bractlets suborbiculate, pubescent, 1 mm. long or less, caducous. Flowers pedicellate, white, about 7 mm. long, the pedicels 1 to 1.5 mm. long. Calyx subtubular, bilabiate, 2.5 to 3 mm. long, sparsely pubescent, the 2 vexillar lobes broad, rounded and adnate, the 2 lateral lobes small andacute, the carinal lobe narrow, acute, twice as long as the others. Petals pink (?), glabrous; standard oblong, hardly auriculate at the base, emarginate, the lobes rounded at the apex, the claw 1.2 mm. long, the blade 5.5 mm. long, 3.3 mm. broad; wings oblique, obovate, auriculate on the vexillar margin at the base, obtuse at the apex, the claw about 1.5 mm. long, the blade 4.5 to 5 mm. long, about 2 mm. broad; carinal petal subfalcate, auriculate on the vexillar side, subacute, the claw as in the wings, the blade 3.2 mm. long, 1.5 mm. broad. Stamens 10, monadelphous, alternately long and short, glabrous. Pistil about 5 mm. long, glabrous, the ovary stipitate, 1 or 2-ovulate, the style slightly arcuate, truncate at the apex.

Legume ovate-oblong, membranous, attenuate at the base in a short, slender stipe, rounded at the apex, 1-seeded, 4.5 to 6 cm. long, 1.5 to 1.7 cm. broad, glabrous. Seeds immature.

Type in the U. S. National Herbarium, no. 571750, collected at Yaxcaba, Yucatán, Mexico, 1895, by G. F. Gaumer (no. 721).

According to a communication of Dr. Millspaugh, the fruits just described, which bear the no. 57934, were collected at a different place by Dr. Gaumer but referred to the above species, under no. 721.

The Maya name of these pods is "Kuxub-tooch," that of the type specimens "cibix."

8. Dalbergia mexicana Pittier, sp. nov.

Branchlets terete, finely striate, ferruginous-puberulous, glabrate.

Leaves 9 to 11-foliolate, the rachis terete, slender, sparsely ferruginous-pubescent, 5 to 7 cm. long. Leaflets subcoriaceous, the petiolules ferryginous-hairy, about 2 mm. long, the blades ovate, or sometimes suborbicular or obcordate, rounded at the base, rounded-emarginate at the apex, 1 to 4 cm. long, 1 to 2 cm. broad, dark green, lustrous, reticulate, glabrous or sparsely ferruginous, reticulate and sparsely pubescent beneath, the costa subimpressed on both faces, the veins prominulous above, obsolete beneath.

Inflorescences axillary, very short (not over 2 cm. long), few-branched, the ramifications subcymose, the rachis ferruginous-hairy. Bractlets ovate, acute, hairy, not over 0.5 mm. long. Flowers pedicellate, about 5 mm. long,

the pedicels hairy, 1 mm. long or less. Calyx cupulate, 2 to 3 mm. long, sparsely hairy at the base, more so on the lobules; vexillar lobules subacute and broad, lateral lobules small, acute, close to the carinal one and separated from the former by deep sinuses; carinal lobule subulate, twice as long as the vexillar ones. Petals glabrous; standard obovate, subbiauriculate at the base, slightly emarginate at the apex, the claw 1.2 mm. long, the blade 4.2 to 4.6 mm. long, 3 to 3.3 mm. broad; wings obovate, rounded-auriculate on the vexillar side, subauriculate on the carinal side, rounded at the apex, the claw 1.2 or 1.3 mm. long, the blade about 4 mm. long, 1.7 or 1.8 mm. broad; carinal petals obovate, auriculate on the vexillar side, rounded at the apex, the claw 1.3 to 1.5 mm. long, the blade about 3 mm. long, 1.5 mm. broad. Stamens 10, monodelphous, the tube open above, glabrous. Pistil 4.8 mm. long, the ovary minutely pubescent on the margins, 2 to 3-ovulate, the style arcuate, glabrous, the stigma inconspicuous.

Type in the John Donnell Smith Herbarium, collected in Mexico, without definite locality, by E. Kerber (no. 434).

9. Dalbergia campecheana Benth. Journ. Linn. Soc. **4:** Suppl. 37. 1860.

TYPE LOCALITY: Campeche, Mexico.

SPECIMENS EXAMINED:

GUATEMALA: Aquascalientes, 1909, *Deam* 6125.

Mr. J. Donnell Smith identified these specimens with Bentham's above named species. This, however, seems to have larger leaves, with 7 to 19 almost sessile leaflets, while in Deam's specimens these are 9 to 11 and petiolulate. The other characters seem to agree.

10. Dalbergia brownei (Jacq.) Urban, Symb. Antill. **4:** 295. 1905.

Amerimnon brownei Jacq. Enum. Pl. Carib. 27. 1760.

Dalbergia amerimnum Benth. Journ. Linn. Soc. **4:** Suppl. 36. 1860.

TYPE LOCALITY: Jamaica.

SPECIMENS EXAMINED:

VENEZUELA: Puerto Cabello, 1874, *Kuntze* 1721.

COLUMBIA: Negüangüe, on the coast between Santa Marta and Rio Hacha, 1898, *H. H. Smith* 1750. Dagua Valley, Cauca, altitude 25 meters, *Triana* 1130.

PANAMA: Providence Island, Bocas del Toro, 1885, *Hart* 182. Beach between Fató and Playa Damas, 1911, *Pittier* 3834. Rio Grande swamps, near Panama City, *Hayes*. La Palma, southern Darién, 1914, *Pittier* 6613. Coiba Island, *Seemann* 626.

COSTA RICA: Ceibo River near Buenos Aires, altitude 200 meters, 1892, *Tonduz* 6675. Santo Domingo de Osa, 1896, *Tonduz* 9892.

NICARAGUA: San Juan del Norte, 1895, *Pittier* 9658.

GUATEMALA: Boca del Polochic, Department Izabal, 1889, *J. D. Smith* 1708. Livingston, 1906, *von Tuerckeim* II. 1216.

MEXICO: Veracruz, 1910, *Adole* (?). Tampico, 1898, *Pringle* 5764, 6809. Rincón Antonio, Oaxaca, 1910, *Orcutt* 3263.

Several species may be included under this name. According to Bentham, it is a tree; Tonduz describes it as a shrub (arbrisseau); while H. H. Smith says it is a "twining plant, reaching 30 feet, with a prickly main stem and 2 inches or more in diameter." In my own notes, no. 3834 is described as "a shrubby vine, with white flowers," and no. 6613, as a small tree branching from

the base." The only fruits at hand differ a little from Bentham's description, and in Donnell Smith no. 1708, from Guatemala, I find the petals narrower, the standard auriculate, the ovary 5-ovulate and other small differences.

Although distinctly characteristic of the strand formation, *Dalbergia brownei* is sometimes found far above sea-level. H. H. Smith observed it, for instance, up to about 700 meters in Santa Marta.

11. Dalbergia ecastophyllum (L.) Taub. in Engl. & Prantl, Pflanzenfam. **3**[3]: 335, 1894.

Hedysarum ecastophyllum L. Syst. ed. 10, **2**: 1169. 1759.

Ecastaphyllum brownei Pers. Syn. **2**: 277. 1807.

TYPE LOCALITY: West Indies.

SPECIMENS EXAMINED:

TRINIDAD: Port of Spain, 1874, *Kuntze* 764.

VENEZUELA: Paparo, mouth of Rio Grande del Tuy, Barlovento, Miranda, 1913, *Pittier* 6349.

COLOMBIA: Santa Marta, 1914, *Sinclair*.

PANAMA: Chagres, 1854, *Fendler* 315. Colon, *Hayes* 155. Without definite locality, 1874, *Kuntze* 764.

COSTA RICA: Boca Banano, 1895, *Tonduz* 9156. Diquis River, 1891, *Tonduz* 4014. Punta Mala, in the Diquis delta, 1892, *Tonduz* 6775. Santo Domingo de Osa, 1896, *Tonduz* 9892.

GUATEMALA: Puerto Barrios, 1905, *Deam* 59.

HONDURAS: Puerto Sierra, 1903, *Wilson* 248. Ruatán Island, 1886, *Gaumer*.

BRITISH HONDURAS: Manatee Lagoon, 1906, *Peck* 463.

Dalbergia ecastophyllum has also been reported from many localities from Rio de Janeiro northwards and including the Guianas on the Atlantic seaboard of South America, from all over the West Indies, and from Florida. It is worthy of notice that this shrub does not seem to have been recorded from Mexico.

12. Dalbergia monetaria L. f. Suppl. 317. 1781.

TYPE LOCALITY: Surinam.

SPECIMENS EXAMINED:

FRENCH GUIANA: Karouany, *Sagot* 159.

VENEZUELA: Bosque de Catuche, above Caracas, 1913, *Pittier* 6297.

PANAMA: Rio Sirri, Trinidad Basin, province of Colón, near sea-level, 1911, *Pittier* 4029.

HONDURAS: Tela River, near Puerto Sierra, 1903, *Wilson* 77. Laguna Quemada, Atlantic Coast, 1903, *Wilson* 627.

GUATEMALA: Puerto Barros, 1905, *Deam* 70.

This species is scarcer in Central America than either *D. brownei* or *D. ecastophyllum*. It does not figure in the Biologia Centrali-Americana, and, since the publication of this work, has been reported only from a few localities as shown above, all on the Atlantic seaboard, from Guatemala southeastwards. It is found also in the West Indies and on the eastern watershed of South America as far south as the Amazon basin. It penetrates far into the interior along the main rivers, and in the vicinity of Caracas reaches an altitude of about 1200 meters.

Unless it has been incorrectly stated, the habit of this species is very variable. Some report it as a shrub or small tree up to 3 meters high; Bentham[3] says "caulis lignosus vulgo scandens;" and the notes corresponding to my no. 6297 from near Caracas are as follows: "a large vine, often 15 cm. in diam. at the base and climbing to the top of the highest trees." The shape of the fruit is also different in specimens from different localities, although I have never seen the oblong type reproduced in plate 63 of the work just cited. With reference to this plate it may be opportune to mention that although Bentham indicates only 9 stamens, as always found by myself, he gives two illustrations of the androecium of *D. monetaria*, each with 10 stamens.

13. Dalbergia calycina Benth. Journ. Linn. Soc. **4**: Suppl. 35. 1860.

TYPE LOCALITY: Guatemala (*Friedrichsthal*).

14. Dalbergia hypoleuca Pittier, sp. nov.

Tree; young branchlets ferruginous-pubescent.

Leaves 7 to 11-foliolate, the rachis terete, pubescent, glabrescent, 10 to 20 cm. long. Leaflets coriaceous, often opposite or subopposite, the petiolules canaliculate, grayish-pubescent, 5 to 7 mm. long, the blades ovate or ovate-oblong, rounded at the base, obtuse and subretuse at the apex, 3 to 7 cm. long, 2 to 3 cm. broad, glabrous and finally reticulate with the venation prominulous above, beneath grayish or whitish, minutely pubescent, with the costa very prominent and the veins slightly so; margins strongly revolute.

Inflorescence axillary or terminal. Flowers not known.

Legume coriaceous, glabrous, long-stipitate, rounded-attenuate at the base, rounded and mucronulate at the apex, 1-seeded and then 8 cm. long and 2 cm. broad, or 2 to 5-seeded and up to about 16 cm. long, the breadth varying between 1.7 and 1 cm.

Type in the John Donnell Smith Herbarium, collected at El Escobal, near Atenas, Costa Rica, by Federico Golcher. Represented also in the U. S. National Herbarium (no. 716263) by the same collection, without date, and numbered 1747, which probably corresponds to the series of the Instituto físico-geográfico.

This is the Costa Rican *Cocobola*, equal in value to that of Panama, but even scarcer. It is probably a close relative of the latter, but the leaflets are less numerous, and the pods much narrower.

15. Dalbergia granadillo Pittier, sp. nov.

Tree. Leaves 7 to 13-foliolate, the rachis terete, at first pubescent, 9 to 17.5 cm. long. Leaflets submembranous, often subopposite, the petiolules sparsely pubescent or glabrescent, canaliculate, 4 to 5 mm. long, the blades suborbiculate or ovate, broadly rounded at the base, obtuse or subacuminate at the apex, 3 to 5.5 cm. long, 2 to 4 cm. broad, glabrous and reticulate with the venation prominulous above, glabrous except on the prominent, sparsely pubescent costa, and the veins prominulous, beneath; margins not revolute.

Inflorescence paniculate, axillary or terminal, the rachis few-branched, ferruginous-pubescent. Flowers few. Calyx cupulate, ferruginous-pubescent, persistent. Other floral details not known.

[3] In Mart. Fl. Bras. **15**[1]: 229. 1862.

Legume lanceolate, long-stipitate, attenuate at the base, acute at the apex, glabrous, lustrous, 1-seeded and about 9 cm. long and 1.8 or 2 cm. broad, or 2 to 4-seeded and then up to 17.5 cm. long. Seeds oblong-reniform, not mature.

Type in the Gray Herbarium, collected at El Tibor, in the valley of the Balsas River (between the States of Guerrero and Michoacan), Mexico, August 22, 1898, by E. Langlassé (no. 294).

Like *D. retusa* and *D. hypoleuca*, this species furnishes a precious wood, which is hard, fine, and red-veined, and is known locally as *granadillo*.

The specimens at hand are hardly satisfactory for a description, but they belong to a section heretofore not known to be represented in Mexico, and differ from the other Middle American species of the group in the shape, consistence and indument of the leaflets, and in the shape and appearance of the pods. It is consequently pretty safe to consider them as corresponding to a type specifically distinct.

16. Dalbergia retusa Hemsl. Diagn. Pl. Nov. **1**: 8. 1878.

TYPE LOCALITY: Paraiso, Panama (*Hayes* 642).

SPECIMENS EXAMINED:

PANAMA: Penonomé, Coclé, 1908, *Williams* 425. Chagres River above Alhajuela, 1911, *Pittier* 3511. Vicinity of La Palma, southern Darién, 1914, *Pittier* 6606.

COSTA RICA: Salinas Bay, between the littoral plain and La Cruz de Guanacaste, 1908, *Pittier* 2737.

This is the Panama "cocobola," a hard wood very well known commercially and obtained probably from several species of the same genus. I have seen no specimens from the type collection, but ours agree generally with the description. The leaflets, however, are more numerous and not usually retuse and the flowers seem to be smaller.

In Panama this tree has been exploited with such diligence as to have become very scarce in the central and western districts. In 1914 the more important logging camps were at Sumacate and Rio Congo in Darien.

17. Dalbergia lineata Pittier, sp. nov.

Large deciduous tree with rounded crown; young branchlets minutely fuliginous-pubescent.

Leaves 8 to 15-foliolate, the rachis 8 to 20 cm. long, more or less fuliginous-pubescent. Leaflets petiolulate, at first membranous, often opposite or subopposite, the petiolules grayish-hairy, about 7 mm. long, the blades ovate or oblong, cuneate or attenuate at the base, obtuse at the apex, 4 to 8 cm. long, 2 to 3.5 cm. broad, glabrous above, with the costa and veins prominent, densely grayish-pubescent beneath. Stipules ovate, acute, fuliginous-pubescent without, up to 7 mm. long and 3 mm. broad, very caducous.

Inflorescences paniculate, axillary or terminal, few-flowered, the rachis fuliginous-pubescent, 4 to 15 cm. long. Bracts and bractlets fuliginous-hairy, very caducous, the latter oblong, obtuse, not over 1 mm. long, inserted in pairs close to the calyx. Flowers about 16 mm. long, the pedicels densely fuliginous-hairy, about 3 mm. long. Calyx cupulate, 5 to 6 mm. long, densely pubescent, the vexillar lobes broader, equal in length to the lateral ones, the

carinal lobe linear-apiculate and longer. Petals white, delicately purple-lined, glabrous; standard strongly reflexed, ovate, attenuate at the base, emarginate at the apex, the claw 3 mm. long, the blade 10 mm. long, 8.5 mm. broad; wings obovate, oblique, auriculate on the vexillar side, the claw 3.5 mm. long, the blade 11.5 mm. long, 4.5 mm. broad; carinal petals falcate, auriculate on the vexillar side, obtuse at the apex, the claw as in the wings, the blade about 10 mm. long, 4 mm. broad. Stamens 10, monadelphous, alternately long and short. Pistil about 13 mm. long, glabrous, the ovary long-stipitate, linear, 4 to 6-ovulate; style strongly arcuate; stigma capitellate, inconspicuous.

Type in the U. S. National Herbarium, no. 577918, collected at Nicoya, Costa Rica, April, 1900, by A. Tonduz (no. 13969).

A specimen (Inst. fis.-geogr. n. 13887), obtained by the same collector from the forest of Nicoya, is probably the same species. However, the specimens are leafless and floral panicles larger and many-flowered. Mr. Tonduz says that the tree they proceed from is a preponderant one in the forests of the peninsula, being gregarious and giving a characteristic bluish-gray color to the forests in April, the flowering time.

The affinities of this species are evidently with *Dalbergia retusa* Hemsley.

ELECTRICITY.—*Electromotive force of cells at low temperatures.*[1] G. W. VINAL AND F. W. ALTRUP, Bureau of Standards.

The practical importance of a knowledge of the electromotive behavior of dry cells and storage batteries at low temperatures has arisen from their use in the Arctic and at high altitudes. In June, 1921 the Department of Terrestrial Magnetism of the Carnegie Institution, of Washington, through Dr. S. J. Mauchly, requested the Bureau of Standards to furnish information in answer to the following questions: (a) What is the open circuit voltage of dry cells at approximately 0° Fahrenheit and below? (b) Are dry cells fit for use after they have been frozen and thawed out again? Since there was no reliable information available on this subject, experimental work was undertaken which included observations on storage batteries also. In the first experiment the temperature range was extended to −72° C. and as the open circuit voltage of the cells was not materially changed by cooling them to this temperature, the work was extended to −170° C. because of the theoretical interest in the application of the Gibbs-Helmholtz and Nernst equations to these cells.

Two methods of cooling the cells were employed. For the range +25° to −72° C., the cells were submerged in a gasoline bath to which small amounts of carbon dioxide snow were added gradually until the

[1] Published by permission of the Director of the Bureau of Standards. Received January 6, 1922.

lowest temperature attainable by this means was reached, when an excess of the snow was packed around the cells. For the range $+20°$ C. to $-170°$ C. liquid air was used for cooling. The dry cells were placed in a double walled glass jacket similar to a Dewar vessel, but having air at atmospheric pressure between the walls. This was submerged in liquid air contained in a larger Dewar flask. The storage cell, contained in a glass test tube, was similarly arranged with the addition of a ground-cork packing to protect it from breakage. By this means the cooling was gradual, about 2 hours being required for the cells to fall from room temperature to the lowest temperature available.

The temperature was measured by a thermocouple of standardized constantan and copper wire. Since it was not practicable to insert the thermocouple in the dry cells of which the e.m.f. was measured, the thermocouple was placed at the center of a similar dry cell which was grouped symmetrically with the other cells. The temperature of the storage cell was measured by placing the thermocouple, protected by a thin-walled glass tube, in the electrolyte between the positive and negative plates of the cell. The electromotive forces of the thermocouples were read on a high resistance potentiometer.

The dry cells measured were $^3/_4$ inch diameter $\times$ $2^1/_8$ inch high, taken from flashlight batteries of a well known make. A few experiments on silver chloride dry cells were made also. The storage cells were made by cutting strips of suitable size from the pasted plates of an automobile starting and lighting battery. These were placed in test tubes about 1 inch in diameter with perforated hard rubber separators and a few glass beads. The electrolyte was adjusted to a specific gravity of 1.275 to 1.280 at the end of 5 days of continuous charging at 0.4 ampere.

The voltage of the cells during test was measured by 3 different methods but the open-circuit measurements at the lowest temperatures could be made only by an electrometer. This instrument was loaned to us by the Department of Terrestrial Magnetism. The open circuit voltages were also measured on a 20,000-ohm potentiometer which afforded a very sensitive method before the cells were frozen although after this it was nearly useless. A voltmeter having a scale of 2.5 volts and a resistance of 25,000 ohms was used for some of the measurements.

The results of experiments with dry cells of the ordinary type are shown in Table 1 and Fig. 1. Curves A and B represent the open-

circuit voltages as measured for two different cells by the electrometer and the potentiometer. Curves C, D, E and F represent the terminal voltage when the cells were discharging through 25,000, 100, 25 and 4 ohms, respectively. The curves indicate the existence of a critical point at about −21° C.

The open-circuit voltage curves indicate that changes in the temperature coefficient occur at certain temperatures. Between +26° and 0° C. the coefficient was found to be constant and somewhat less than a millivolt per degree. The coefficient is positive, that is, increase in temperature is accompanied by increase in voltage. Between 0°

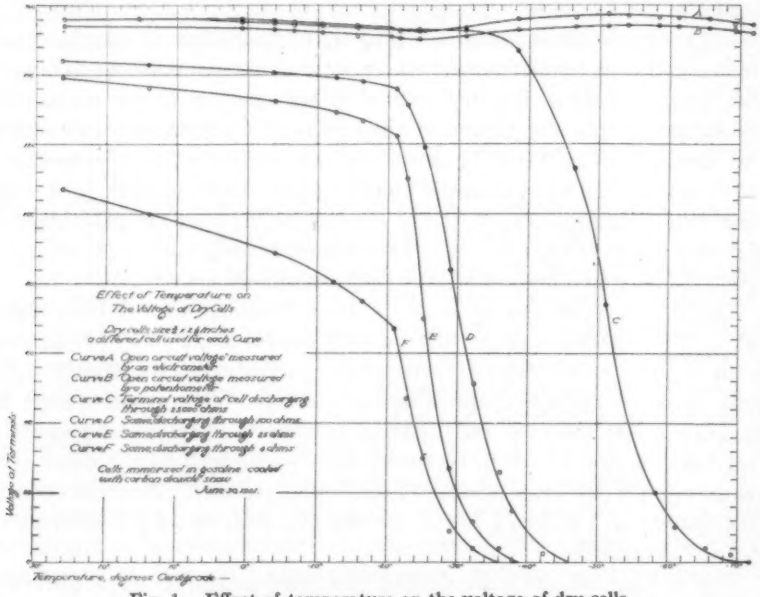
Effect of Temperature on
The Voltage of Dry Cells
Curve A. Open circuit voltage measured by an electrometer
Curve B. Open circuit voltage measured by a potentiometer
Curve C. Terminal voltage of cell discharging through 25,000 ohms
Curve D. Same discharging through 100 ohms
Curve E. Same discharging through 25 ohms
Curve F. Same discharging through 4 ohms
Cells immersed in gasoline cooled with carbon dioxide snow
Volts
Temperature, Degrees Centigrade

Fig. 1. Effect of temperature on the voltage of dry cells.

and −20° C. the coefficient is still positive, but larger. At −20.4° C. a break occurs. The temperature coefficient becomes much larger during the next few degrees and then changes to negative at about −24°. At −54° the coefficient again becomes positive. It is interesting to note that at −54° C. the voltage is higher than at ordinary temperatures.

Curves C, D, E and F show that the ordinary dry cell can deliver current down to about −20° C., below which the voltage falls off rapidly to zero.

Silver chloride dry cells were measured in a similar manner, and the open circuit voltages are given in Table 1. When the voltage was measured by the 25,000-ohm voltmeter, however, the terminal voltage began to fall rapidly from 0° C. downward. At −10° it was 0.9 volt, and from this point it decreased nearly linearly to 0.05 volt at −50°.

Experiments were also made to determine the voltage of storage cells within the range +25° to −72° C., using the electrometer, the potentiometer and the voltmeter to measure the voltage. As freezing did not occur within this range, the potentiometer gave the most accurate results and these are given in Table 1, but the results of all

TABLE 1.

OPEN CIRCUIT VOLTAGES OF CELLS FOR VALUES BELOW −70° C. SEE FIG. 2

Temperature	Ordinary* dry cell	Storage* cell	Silver** chloride cell
°C.	Volts	Volts	Volts
20	1.540	2.116	1.06
10	1.537	2.113	1.05
0	1.533	2.111	1.04
−10	1.523	2.107	1.03
−20	1.512	2.103	1.02
−30	1.508	2.100	1.01
−40	1.530	2.096	1.00
−50	1.540	2.092	0.99
−60	1.540	2.087	0.98
−70	1.526	2.081	0.97

* Based on potentiometer readings.

** Interpolated values based on electrometer readings.

methods were in good agreement. The temperature coefficient was small and constant. This fact permitted an accurate estimate of the temperature coefficient to be made since the cell had sufficient time for thermal equilibrium to be established at the beginning and end of this range. The temperature coefficient was found to be 0.000398 volt per degree C.

It is interesting to compare this result with the value computed from the available thermochemical data and the Gibbs-Helmholtz equation. This equation is usually written

$$Q = W - T\frac{dW}{dT} \qquad (1)$$

where Q is the heat of the reaction; W the available work and T the absolute temperature. This equation is applicable to a reversible cell in which the passage of current does not involve any appreciable

change in volume. If E denotes the open circuit voltage of the cell W equals 96500 E volt-coulombs[2] for 1 equivalent. Q expressed in calories may be converted to voltcoulombs by multiplying by 4.183 and the equation becomes:

$$\frac{dE}{dT} = \frac{1}{T}\,(E - 0.000021674\ Q). \qquad (2)$$

Both E and Q are dependent on the concentration of the electrolyte which for this experiment was of 1.280 sp. gr. The value of E corresponding to the initial value T was observed directly. The value for Q may be calculated from published thermochemical data.

The commonly accepted reaction of the lead accumulator during discharge may be described by the following equation:

$$\left.\begin{array}{l}\text{Positive plate,}\quad PbO_2 + H_2SO_4 \\ \text{Negative plate,}\quad Pb + H_2SO_4\end{array}\right\} + n.H_2O \longrightarrow 2PbSO_4 + (n+2)H_2O$$

where n is the number of molecules of water to 2 molecules of sulphuric acid in the original solution. The corresponding thermochemical equation is

$$PbO_2 + Pb + 2H_2SO_4 + n.H_2O = 2PbSO_4 + (n+2)H_2O + Q_n$$

where Q_n, the heat of the reaction, depends on the dilution of the acid, which is fixed by n. Since the chemical reaction must take H_2SO_4 from the dilute electrolyte, the energy represented by Q_n for other strengths of acid will be less in amount by the quantity of heat evolved by dilution of the acid, or Q_n will be greater if the concentration is greater.

Values for Q have been determined by Streinz[3] and Tscheltzow[4] to be 87000 and 88600 calories, respectively. The mean of their determinations is 87800 calories. Dolezalek[5] states that these values apply to dilute sulphuric acid (1 molecule of H_2SO_4 to about 400 molecules of H_2O) and hence a correction for the heat of dilution is necessary. The heat of dilution[6] of the acid solution from a specific gravity of 1.280 as used in our experiment to the concentration equivalent to 1 molecule of acid to 399 mols.of water is 2210 calories per gram molecule. Two gram molecules are involved and hence the value for

[2] The value 96500 coulombs is based on recent determinations with the silver and iodine voltameters by Vinal and Bates at the Bureau of Standards Sci. Paper No. 218.

[3] Wied. Ann. 53: 698. 1894.

[4] Comptes Rendus 100: 1458. 1885.

[5] *Theory of the Lead Accumulator*, p. 29.

[6] Thomsen's data, Landolt and Bornstein tables, ed. 4, p. 885.

the heat of the reaction for an electrolyte of 1.280 specific gravity is $87800 + 4420 = 92220$ calories.

The value for E at 25° C. and electrolyte of specific gravity 1.280 was 2.120 volts. The temperature, 25° C., corresponds to 298° absolute. Substituting these values for T, E and Q in equation (2) the value for the temperature coefficient dE/dT is found to be 0.0004.07 The results of the experiment showed a decrease in the open circuit voltage of 0.0386 volt when the temperature was decreased 97° from which $dE/dT = 0.000398$.

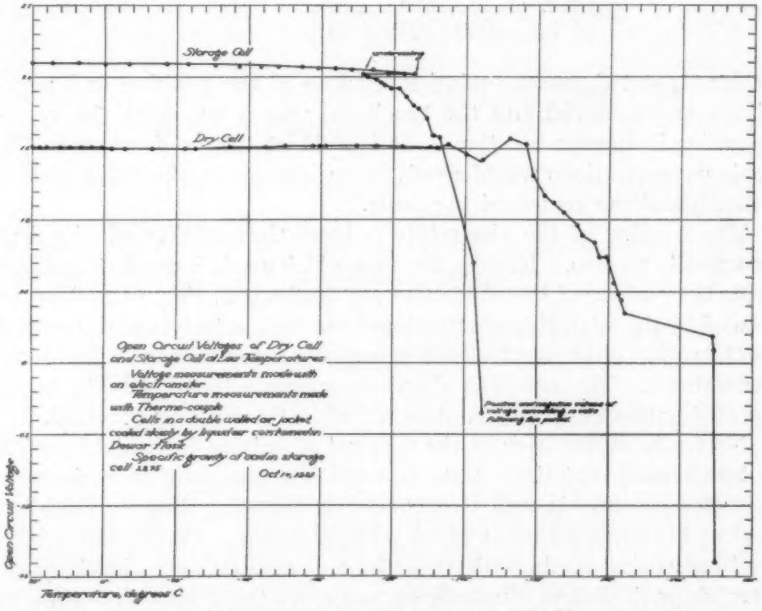
Storage Cell
Dry Cell
Open Circuit Voltages of Dry Cell and Storage Cell at Low Temperatures
Voltage measurements made with an electrometer
Temperature measurements made with Therme-couple
Cells in a double walled or jacket cooled slowly by liquid air contained in Dewar Flask
Specific gravity of sodium storage cell 1.275
Oct. 11, 1921
Open Circuit Voltage
Temperature, degrees C

Fig. 2. Open circuit voltages of dry cell and storage cell of low temperatures.

The agreement of this observed value with that calculated from thermochemical data is better than would be expected and gives a striking proof of the validity of the Gibbs-Helmholtz equation over a wide range of temperature.

A second series of measurements extending the temperature range down to −170° C. was then made. Only the electrometer readings are of value at this low temperature. The results on a dry cell and a storage cell are shown graphically in Fig. 2. These are the open circuit voltages measured electrostatically. The storage cell showed

marked under-cooling of the electrolyte before freezing began. The dry cell showed a considerable increase in voltage at −112° C. over the normal value. The most remarkable facts are the reversal of voltages and the extraordinarily large values of voltage exhibited by the storage cell, exceeding ten volts at the lowest temperatures. The current was of course vanishingly small.

Nernst's equation applied to the storage battery in accordance with Liebenow's theory[7] is as follows:

$$E = \frac{RT}{2} \ln \frac{C_p C_n}{[Pb^{++}][PbO^{--}]}$$

where C_p and C_n are the solution tensions of the positive and negative active material and the bracketed values represent the corresponding ionic concentrations. It is evident that a decrease in the ionic concentrations would result in an increase in the value of E if other quantities remained the same.

The freezing of the electrolyte reduces the mobility of the ions practically to zero. If, then, the ions which are in immediate contact with the surface of the electrodes are discharged, they cannot be replaced by the migration of other ions from the electrolyte and the effect in the region of the electrodes is essentially a decrease in the ionic concentrations. The equation therefore suggests the possibility of increased values of E as was observed after the freezing occurred.

No ready explanation of the reversal of voltage is available unless it be assumed that the variation of solution tension of each electrode with temperature is such that curves representing them would intersect at the temperature at which reversal occurs. Pressure may have had something to do with the voltage variations since the electrometer showed violent fluctuations whenever the frozen electrolyte of the storage cell "ticketed." Ice below the freezing temperature sometimes makes a similar ticking sound.

The genuineness of the reversed voltage was shown by the following observations: The dry cell after showing a steady reversed voltage of about 1.4 volts was removed from the liquid air and in the course of a few minutes, the reversed voltage decreased steadily, passed through zero, and increased to a normal positive value. Secondly, the potentiometer used for simultaneous measurements with the electrometer on the storage cell retained enough sensibility to show that the

[7] Zeitschr. f. Elektrochem. 3: 525. 1897.

potential was reversed at the same time that the electrometer showed a reversed reading.

All of the cells, including the ordinary type of dry cell, the silver chloride cells and the storage cells appeared to be entirely normal after being thawed out. The glass test tube containing the storage cell was not broken.

The experiments in the range 25° to −72° C. answer completely the practical questions which prompted the investigation. The thermodynamic theory as expressed in the Gibbs-Helmholtz equation is accurately confirmed by the measurements on a storage cell. At temperatures down to −170° C. points of theoretical interest were found. These suggest that potential differences of normal value at ordinary temperatures may be greatly magnified at extremely low temperatures when the current is vanishingly small. High atmospheric potentials sometimes observed may have some relation to this effect.

We wish to thank Dr. L. A. Bauer, Director of the Department of Terrestrial Magnetism, for his courtesy in lending us the electrometer and Dr. Mauchly for assistance in taking some of the observations, also Dr. E. Buckingham for valuable suggestions.

ABSTRACTS

GEOLOGY.—*Deposits of manganese ore in Montana, Utah, Oregon, and Washington.* J. T. PARDEE. U. S. Geol. Surv. Bull. No. **725-C.** Pp. 141–243, pls. 4, figs. 11. 1921.

The demand for manganese, created by the World War, caused the development of many deposits in the States mentioned. Those at Phillipsburg and Butte, Montana, which became the most productive in the United States are parts of the quartz veins that carry silver and zinc. They were formed in Tertiary time by the replacement of country rock by manganiferous carbonates and silicates that emanated from intrusive granitic magmas. The superficial parts of the deposits have been oxidized without noteworthy changes in their manganese content.

In Utah deposits of manganese ore related to metalliferous veins are found in several of the mining districts. In the Little Grande district flat lying, lens-like or tabular masses of manganese oxides, found at a certain horizon in the Mesozoic McElmo formation, were deposited originally as carbonate associated with limestone, gypsum and other sediments. In the later Tertiary they were uncovered by erosion, oxidized and locally concentrated into workable bodies.

In the Lake Creek district, Oregon, manganese oxides fill cracks, pores, or other cavities in a Tertiary volcanic tuff. The manganese was deposited by descending solutions, but its origin is obscure. Other deposits formed by

replacement of country rock by carbonate or silicate minerals occur in southwestern and northeastern Oregon.

In Washington, in the Olympic Mountains and the northern part of the Puget Sound region, are uncommon deposits that consist chiefly of bementite a silicate of manganese. Associated with the bementite are quartz, rhodonite, manganocalcite and unidentified oxides of manganese. Hematite forms separate though closely related bodies. Locally the bementite is cut by veinlets of neotocite, a kindred silicate, and in places it contains specks and flakes of native copper. The deposits are thought to be manganiferous marine sediments, greatly altered by regional metamorphism. J. T. P.

GEOLOGY.—*Deposits of chromite in California, Oregon, Washington and Montana.* J. S. DILLER, L. G. WESTGATE and J. T. PARDEE, U. S. Geol. Surv. Bull. No. **725-A.** Pp. 84 with maps, 5 plates and 23 figures.

During the World War it became necessary to determine as closely as possible the chromium resources of the country. It was demonstrated that the United States had reserve deposits adequate to supply a war demand for several years. Now that the war is over the country is conserving its domestic supplies by employing higher grade and cheaper ore from foreign countries.

The first paper "Chromite in the Klamath Mountains, California and Oregon" discusses in detail the occurrence and origin of chromite, and in this respect serves as an introduction to all the papers that follow.

In the Klamath Mountains chromite deposits have three distinct structures, even granular, nodular and banded. The nodular is concretionary and the banded is gneissoid. The even granular deposits are the most abundant and widely distributed in California, Oregon and Washington. The nodular structure occurs in California and Oregon and the banded structure in California and Montana. In California the banded structure is distinctly associated with gneiss; and in Montana it occurs in a remarkable dike of peridotitic rock. J. S. D.

GEOLOGY.—*Geology of the vicinity of Tuxedni Bay, Cook Inlet, Alaska.* FRED H. MOFFIT. U. S. Geol. Surv. Bull. **722-D.** Pp. 7, with geologic map, 1921.

The paper describes the marine sedimentary rocks of a small area on the west side of Cook Inlet where a section of Middle and Upper Jurassic beds is particularly well displayed. These beds comprise a succession of sandstones, arkoses, shales, and conglomerates, derived in large part from a nearby ancient land mass where granitic rocks were abundant, and reach a thickness of possibly 9000 feet. The beds are especially fossiliferous in the lower part and are there characterized by an abundance of plant remains intermingled with the marine invertebrate forms. The jurassic beds are faulted against the volcanic rocks of the Aleutian Range on the west and dip at angles ranging from 10° to 25° south-southeast or toward Cook Inlet.

Petroleum seeps are known in these rocks in the vicinity of Iniskin Bay about 40 miles southwest of Tuxedni Bay but were not seen in the area which is described. F. H. M.